

## The First Suzuki Cross-Coupling of Aryltrimethylammonium Salts.

Simon B. Blakey and David W. C. MacMillan\*

*Division of Chemistry and Chemical Engineering, California Institute of Technology,  
Pasadena, California 91125*

### Supporting Information

**General Information.** Commercial reagents were purchased from Aldrich or Strem and used as supplied. Reactions were conducted using standard drybox techniques. Non-aqueous reagents were transferred under argon via syringe. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Dioxane was distilled from sodium benzophenone ketyl and then degassed using the freeze-pump-thaw method (4 cycles) prior to use. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel 63 according to the method of Still.<sup>1</sup> Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by fluorescence quenching or iodine stain.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 300 spectrometer (300 MHz and 75 MHz) as noted, and are internally referenced to residual protio solvent signals. Data for <sup>1</sup>H NMR are reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration and coupling constant (Hz). Data for <sup>13</sup>C NMR are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm<sup>-1</sup>). Mass spectra were obtained on a JEOL JMS-600H spectrometer. Melting points were recorded on a Thomas Hoover capillary melting point apparatus, and are uncorrected.

**General Procedure:** A *N,N,N*-trimethylanilinium trifluoromethanesulfonate (0.157 mmol), Ni(COD)<sub>2</sub> (4.3 mg, 0.0157 mmol), IMes-HCl (5.4 mg, 0.0157 mmol), a boronic acid (1.1 or 2 equivalents) and CsF (73 mg, 0.471 mmol) were combined in a 2 dram screw-capped vial containing a magnetic stirrer bar under a nitrogen atmosphere. The vial was sealed with a cap containing a teflon coated septum, removed from the drybox and charged with dioxane (1.0

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<sup>1</sup>Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

mL). The heterogeneous mixture was heated to 80 °C and stirred for 12 h. Upon cooling to r.t., the mixture was filtered through a plug of silica, washing with ethyl acetate. The solvent was removed *in vacuo* and the residue was purified by silica gel chromatography (3–10% ethyl acetate/hexanes) to afford substituted biphenyls.

**4-*n*-Butylbiphenyl (Table 1, entry 8).** Prepared according to the general procedure from *N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and phenylboronic acid (21 mg, 0.172 mmol). Purification by flash chromatography (3% EtOAc/Hexanes) gave the title compound as a colourless oil in 98% yield (32.3 mg, 0.154 mmol), which had physical data identical in all respects to that previously reported.<sup>2</sup>

**4-*n*-Butyl-2'-methylbiphenyl (Table 2, entry 1).** Prepared according to the general procedure from *N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and 2-methylphenylboronic acid (43 mg, 0.314 mmol). Purification by flash chromatography (3% EtOAc/Hexanes) gave the title compound as a colourless oil in 83% yield (29.9 mg, 0.130 mmol), which had physical data identical in all respects to that previously reported.<sup>3</sup>

**4-*n*-Butyl-3'-methylbiphenyl (Table 2, entry 2).** Prepared according to the general procedure from *N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and 3-methylphenylboronic acid (43 mg, 0.314 mmol). Purification by flash chromatography (3% EtOAc/Hexanes) gave the title compound as a colourless oil in 89% yield (32.1 mg, 0.140 mmol).  $R_f = 0.64$  (5% EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (2H, dt,  $J = 8.2, 1.9$  Hz), 7.40 (2H, br m), 7.32 (1H, td,  $J = 7.7, 1.1$  Hz), 7.25 (2H, dt,  $J = 8.2, 1.7$  Hz), 7.15 (1H, br d,  $J = 6.6$  Hz), 2.66 (2H, t,  $J = 7.7$  Hz), 2.42 (3H, s), 1.64 (2H, m), 1.39 (2H, m), 0.95 (3H, t,  $J = 7.1$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  142.1, 141.3, 138.8, 138.4, 129.0, 128.8, 128.0, 127.9, 127.2, 124.3, 35.7, 34.0, 22.8, 22.0, 14.4; IR (film) 3023, 2956, 2927, 2857, 1607, 1588, 1566, 1515, 1484, 1465, 1340, 1377, 1119, 1095, 1018  $\text{cm}^{-1}$ ; HRMS (EI+) found 224.1560,  $\text{C}_{17}\text{H}_{20}$  requires 224.1565.

**4-*n*-Butyl-4'-methylbiphenyl (Table 2, entry 3).** Prepared according to the general procedure from *N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and 4-methylphenylboronic acid (43 mg, 0.314 mmol). Purification by flash chromatography (2%

<sup>2</sup> Rieke, R. D.; Daruwala, K. P. *J. Org. Chem.* **1988**, 53, 2073.

<sup>3</sup> Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, 123, 2719.

EtOAc/Hexanes) gave the title compound as a waxy solid in 95% yield (34.2 mg, 0.149 mmol).  $R_f$  = 0.65 (5% EtOAc/Hexanes); m.p. = 34-36 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (2H, d,  $J$  = 8.2 Hz), 7.51 (2H, d,  $J$  = 8.2 Hz), 7.27 (4H, br d,  $J$  = 8.2 Hz), 2.67 (2H, t,  $J$  = 7.7 Hz), 2.42 (3H, s), 1.66 (2H, m), 1.42 (2H, m), 0.98 (3H, t,  $J$  = 7.1 Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.9, 138.6, 138.5, 136.9, 129.6, 129.0, 127.0, 127.0, 35.7, 34.1, 22.8, 21.5, 14.4; IR (film) 3025, 2957, 2927, 2857, 1498, 1463, 1398, 1378, 1132, 1114, 1041, 1006, 843, 806  $\text{cm}^{-1}$ ; HRMS (EI+) found 224.1567,  $\text{C}_{17}\text{H}_{20}$  requires 224.1565.

**4-*n*-Butyl-2'-methoxybiphenyl (Table 2, entry 4).** Prepared according to the general procedure from *N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and 2-methoxyphenylboronic acid (44 mg, 0.314 mmol). Purification by preparative TLC (5% EtOAc/Hexanes) gave the title compound as a colourless oil in 94% yield (35.3 mg, 0.148 mmol).  $R_f$  = 0.38 (5% EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (2H, d,  $J$  = 8.2 Hz), 7.32 (2H, m), 7.24 (2H, d,  $J$  = 8.3 Hz), 7.02 (2H, m), 3.83 (3H, s), 2.66 (2H, t,  $J$  = 7.7 Hz), 1.67 (2H, m), 1.44 (2H, m), 0.97 (3H, t,  $J$  = 7.1 Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  156.6, 141.8, 135.9, 131.0, 130.8, 129.5, 128.5, 128.3, 121.0, 111.3, 55.8, 35.8, 34.0, 22.9, 14.4; IR (film) 2999, 2956, 2929, 2871, 2856, 1598, 1582, 1516, 1487, 1463, 1456, 1436, 1407, 1378, 1298, 1261, 1239, 1180, 1162, 1122, 1056, 1030, 1006, 932, 852, 834, 794, 752  $\text{cm}^{-1}$ ; HRMS (EI+) found 240.1511,  $\text{C}_{17}\text{H}_{20}\text{O}$  requires 240.1514.

**4-*n*-Butyl-4'-methoxybiphenyl (Table 2, entry 5).** *N,N,N*-Trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol),  $\text{Ni}(\text{COD})_2$  (4.3 mg, 0.0157 mmol), IMes·HCl (5.4 mg, 0.0157 mmol), 4-methoxyphenylboronic acid (0.354 mmol) and  $\text{K}_3\text{PO}_4$  (100 mg, 0.471 mmol) were combined in a 2 dram screw-capped vial containing a magnetic stirrer bar under a nitrogen atmosphere. The vial was sealed with a cap containing a teflon coated septum, removed from the drybox and charged with dioxane (1.0 mL). The heterogeneous mixture was heated to 80 °C and stirred for 12 h. Upon cooling to r.t., the mixture was filtered through a plug of silica, washing with ethyl acetate. The solvent was removed *in vacuo* and the residue was purified by silica gel chromatography (3% EtOAc/Hexanes) to give the title compound as a white crystalline solid in 83% yield (31.3 mg, 0.130 mmol), which had physical data identical in all respects to that previously reported.<sup>4</sup>

<sup>4</sup> Rondeau, R. E.; Berwick, M. A.; Steppel, R. N.; Servé, R. N. *J. Am. Chem. Soc.* **1972**, *94*, 1096.

**4-*n*-Butyl-2',6'-dimethoxybiphenyl (Table 2, entry 6).** Prepared according to the general procedure from *N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and 2,6-dimethoxyphenylboronic acid (58 mg, 0.314 mmol). Purification by flash chromatography (3% EtOAc/Hexanes) gave the title compound as a white crystalline solid in 79% yield (33.4 mg, 0.124 mmol).  $R_f$  = 0.33 (5% EtOAc/Hexanes); m.p. = 59-61 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (5H, m), 6.59 (2H, dd,  $J$  = 8.8, 1.1 Hz), 3.74 (6H, d,  $J$  = 1.7 Hz), 2.66 (2H, t,  $J$  = 7.7 Hz), 1.67 (2H, m), 1.42 (2H, m), 0.97 (3H, t,  $J$  = 7.7 Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  157.8, 141.4, 131.3, 130.9, 128.6, 128.0, 119.6, 104.4, 56.2, 35.9, 33.8, 23.0, 14.5; IR (film) 2999, 2956, 2930, 2870, 2856, 2835, 1589, 1517, 1471, 1432, 1408, 1282, 1245, 1172, 1109, 1038, 1004  $\text{cm}^{-1}$ ; HRMS (EI+) found 270.1617,  $\text{C}_{18}\text{H}_{22}\text{O}_2$  requires 270.1620.

**4-*n*-Butyl-4'-fluorobiphenyl (Table 2, entry 7).** Prepared according to the general procedure from *N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and 4-fluorophenylboronic acid (44 mg, 0.314 mmol). Purification by flash chromatography (3% EtOAc/Hexanes) gave the title compound as a white crystalline solid in 82% yield (29.4 mg, 0.129 mmol).  $R_f$  = 0.56 (5% EtOAc/Hexanes); m.p. = 32-35 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (2H, m), 7.45 (2H, d,  $J$  = 8.2 Hz), 7.25 (2H, d,  $J$  = 7.7 Hz), 7.11 (2H, t,  $J$  = 8.8 Hz), 2.65 (2H, t,  $J$  = 7.7 Hz), 1.63 (2H, m), 1.38 (2H, m), 0.94 (3H, t,  $J$  = 7.1 Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.4 (d,  $J$  = 248 Hz), 142.3, 137.7, 129.1, 128.7, 128.6, 127.0, 115.7 (d,  $J$  = 21.4 Hz), 35.6, 34.0, 22.8, 14.4; IR (film) 3026, 2959, 2930, 2874, 1739, 1605, 1498, 1466, 1395, 1379, 1303, 1265, 1235, 1159, 1126, 1099, 1047, 1008, 848, 819, 782, 738  $\text{cm}^{-1}$ ; HRMS (EI+) found 228.1314,  $\text{C}_{16}\text{H}_{17}\text{F}$  requires 228.1314.

**4-*n*-Butyl-3'-fluorobiphenyl (Table 2, entry 8).** Prepared according to the general procedure from *N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and 3-fluorophenylboronic acid (44 mg, 0.314 mmol). Purification by flash chromatography (3% EtOAc/Hexanes) gave the title compound as a colourless oil in 82% yield (29.4 mg, 0.129 mmol).  $R_f$  = 0.56 (5% EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (2H, dt,  $J$  = 8.2, 1.9 Hz), 7.37 (2H, m), 7.28 (3H, m), 7.02 (1H, m), 2.66 (2H, t,  $J$  = 7.7 Hz), 1.64 (2H, m), 1.39 (2H, m), 0.95 (3H, t,  $J$  = 7.1 Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3 (d,  $J$  = 245 Hz), 142.9, 130.4, 130.3, 129.1, 127.1, 122.8, 122.7, 114.0 (d,  $J$  = 22.0 Hz), 113.9 (d,  $J$  = 21.2 Hz), 35.7, 34.0, 22.8, 14.4; IR (film) 3028, 2957, 2928, 2871, 2857, 1615, 1589, 1565, 1519, 1486, 1477, 1467, 1444, 1404, 1378, 1292, 1182, 1158  $\text{cm}^{-1}$ ; HRMS (EI+) found 228.1320,  $\text{C}_{16}\text{H}_{17}\text{F}$  requires 228.1314.

**4-*n*-Butyl-2'-fluorobiphenyl (Table 2, entry 9).** Prepared according to the general procedure from *N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and 2-fluorophenylboronic acid (44 mg, 0.314 mmol). Purification by flash chromatography (3% EtOAc/Hexanes) gave the title compound as a colourless oil in 98% yield (35.0 mg, 0.154 mmol).  $R_f = 0.56$  (5% EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (2H, dd,  $J = 8.2, 1.7$  Hz), 7.44 (1H, dd,  $J = 8.0, 1.9$  Hz), 7.31 (1H, m), 7.29 (2H, d,  $J = 8.8$  Hz), 7.20 (1H, td,  $J = 7.7, 1.6$  Hz), 7.15 (1H, ddd,  $J = 10.4, 7.7, 1.7$  Hz), 2.67 (2H, t,  $J = 7.7$  Hz), 1.66 (2H, m), 1.41 (2H, m), 0.96 (3H, t,  $J = 7.7$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9 (d,  $J = 247$  Hz), 142.7, 135.2, 130.9 (d,  $J = 3.4$  Hz), 129.1, 128.9 (d,  $J = 22.7$  Hz), 128.9, 128.7, 124.5 (d,  $J = 3.7$  Hz), 116.3 (d,  $J = 22.9$  Hz), 35.8, 34.0, 22.8, 14.4; IR (film) 3027, 2957, 2998, 2871, 1613, 1582, 1520, 1485, 1466, 1452, 1410, 1378, 1252, 1214, 1107, 1042, 1009, 939, 860, 825, 757  $\text{cm}^{-1}$ ; HRMS (EI+) found 228.1322,  $\text{C}_{16}\text{H}_{17}\text{F}$  requires 228.1314.

**4-*n*-Butyl-4'-fluorobiphenyl (Table 2, entry 9).** Prepared according to the general procedure from *N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and 4-fluorophenylboronic acid (44 mg, 0.314 mmol). Purification by flash chromatography (3% EtOAc/Hexanes) gave the title compound as a white crystalline solid in 82% yield (29.4 mg, 0.129 mmol).  $R_f = 0.56$  (5% EtOAc/Hexanes); m.p. = 32-35  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (2H, m), 7.45 (2H, d,  $J = 8.2$  Hz), 7.25 (2H, d,  $J = 7.7$  Hz), 7.11 (2H, t,  $J = 8.8$  Hz), 2.65 (2H, t,  $J = 7.7$  Hz), 1.63 (2H, m), 1.38 (2H, m), 0.94 (3H, t,  $J = 7.1$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.4 (d,  $J = 248$  Hz), 142.3, 137.7, 129.1, 128.7, 128.6, 127.0, 115.7 (d,  $J = 21.4$  Hz), 35.6, 34.0, 22.8, 14.4; IR (film) 3026, 2959, 2930, 2874, 1739, 1605, 1498, 1466, 1395, 1379, 1303, 1265, 1235, 1159, 1126, 1099, 1047, 1008, 848, 819, 782, 738  $\text{cm}^{-1}$ ; HRMS (EI+) found 228.1314,  $\text{C}_{16}\text{H}_{17}\text{F}$  requires 228.1314.

**4-*n*-Butyl-3'-acetylbiphenyl (Table 2, entry 10).** Prepared according to the general procedure from *N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and 3-acetylphenylboronic acid (51 mg, 0.314 mmol). Purification by preparative TLC (5% EtOAc/Hexanes) gave the title compound as a colourless oil in 87% yield (34.5 mg, 0.134 mmol).  $R_f = 0.14$  (5% EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (1H, t,  $J = 1.7$  Hz), 7.91, (1H, dt,  $J = 7.7, 1.7$  Hz), 7.78 (1H, dt,  $J = 7.7, 1.7$  Hz), 7.53 (3H, m), 7.29 (2H, d,  $J = 8.2$  Hz), 2.66 (2H, t,  $J = 7.6$  Hz), 2.66 (3H, s), 1.64 (2H, m), 1.39 (2H, m), 0.95 (3H, t,  $J = 7.7$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  198.3, 142.9, 141.8, 137.7, 137.6, 131.8, 129.2, 127.2, 127.1,

127.0, 35.7, 34.0, 27.2, 22.8, 14.4; IR (film) 3060, 3026, 2957, 2923, 2872, 2858, 1689, 1682, 1608, 1583, 1567, 1517, 1478, 1466, 1436, 1403, 1378, 1357, 1299, 1235, 1174, 1120, 1085, 1018, 962, 916, 840, 794, 694  $\text{cm}^{-1}$ ; HRMS (EI+) found 252.1509,  $\text{C}_{18}\text{H}_{20}\text{O}$  requires 252.1514.

**1-(4-Butylphenyl)-naphthalene (Table 2, entry 11).** Prepared according to the general procedure from *N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and 1-naphthaleneboronic acid (54 mg, 0.314 mmol). Purification by flash chromatography (2% EtOAc/Hexanes) gave the title compound as a colourless oil in 84% yield (34.3 mg, 0.134 mmol).  $R_f$  = 0.62 (5% EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (1H, t,  $J$  = 8.4 Hz), 7.92, (1H, d,  $J$  = 9.3 Hz), 7.87 (1H, d,  $J$  = 7.5 Hz), 7.55 (2H, m), 7.45 (4H, m), 7.33 (2H, d,  $J$  = 6.8 Hz), 2.74 (2H, t,  $J$  = 7.8 Hz), 1.73 (2H, m), 1.47 (2H, m), 1.01 (3H, t,  $J$  = 7.2 Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  142.1, 140.5, 138.2, 134.0, 131.9, 130.1, 128.5, 128.5, 127.6, 127.1, 126.4, 126.1, 125.9, 125.6, 35.8, 34.1, 22.9, 14.4; IR (film) 3045, 2956, 2927, 2857, 1592, 1514, 1505, 1465, 1458, 1438, 1396, 1378, 1337, 1248, 1205, 1186, 1161, 1116, 1021, 963, 843, 831, 797, 776  $\text{cm}^{-1}$ ; HRMS (EI+) found 260.1560,  $\text{C}_{20}\text{H}_{20}$  requires 260.1565.

**4'-Butylbiphenyl-3-carboxylic acid ethyl ester (Table 2, entry 12).** Prepared according to the general procedure from *N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and ethyl-3-(4,4,5,5-tetramethyl-1-3-2-dioxaborolan-2-yl)benzoate (87 mg, 0.314 mmol). Purification by flash chromatography (3% EtOAc/Hexanes) gave the title compound as a colourless oil in 89% yield (34.3 mg, 0.134 mmol).  $R_f$  = 0.31 (5% EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (1H, t,  $J$  = 2.2 Hz), 8.00 (1H, dt,  $J$  = 7.7, 1.1 Hz), 7.77 (1H, dt,  $J$  = 7.7, 1.7 Hz), 7.55 (2H, d,  $J$  = 8.2 Hz), 7.49 (1H, t,  $J$  = 7.7 Hz), 7.27 (2H, d,  $J$  = 8.3 Hz), 4.41 (2H, q,  $J$  = 7.1 Hz), 2.66 (2H, t,  $J$  = 7.7 Hz), 1.63 (2H, m), 1.41 (5H, m), 0.95 (3H, t,  $J$  = 7.1 Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.8, 142.8, 141.5, 137.7, 131.5, 131.2, 129.1, 128.9, 128.2, 128.2, 127.2, 61.4, 35.7, 34.0, 22.8, 14.8, 14.4; IR (film) 2958, 2930, 2872, 1721, 1606, 1586, 1517, 1478, 1466, 1440, 1403, 1391, 1367, 1306, 1269, 1241, 1171, 1109, 1084, 1045, 1022  $\text{cm}^{-1}$ ; HRMS (EI+) found 282.1628,  $\text{C}_{19}\text{H}_{22}\text{O}_2$  requires 282.1620.

**4'-(1-hexenyl)biphenyl-4-carboxylic acid methyl ester (Table 2, entry 13).** 4-(Carboxylic acid methyl ester)-*N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol),  $\text{Ni}(\text{COD})_2$  (4.3 mg, 0.0157 mmol), IMes·HCl (5.4 mg, 0.0157 mmol) and CsF (73 mg, 0.471 mmol) were combined in a 2 dram screw-capped vial containing a magnetic stirrer bar under a nitrogen atmosphere. The vial was sealed with a cap containing a teflon coated septum,

removed from the drybox and charged with a solution of B-(*E*-1-hexenyl)-9-BBN (69 mg, 0.314 mmol) in dioxane (1.0 mL). The heterogeneous mixture was heated to 80 °C and stirred for 12 h. Upon cooling to r.t., the mixture was filtered through a plug of silica, washing with ethyl acetate. The solvent was removed *in vacuo* and the residue was purified by silica gel chromatography (5% ethyl acetate/hexanes) to afford the title compound as a colourless oil in 92% yield (31.5 mg, 0.144 mmol).  $R_f$  = 0.5 (10% EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (2H, d,  $J$  = 8.8 Hz), 7.38 (2H, d,  $J$  = 8.8 Hz), 6.38 (2H, m), 3.90 (3H, s), 2.22 (2H, dt,  $J$  = 7.1, 6.6 Hz), 1.42 (4H, m), 0.92 (3H, t,  $J$  = 7.2 Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 142.6, 134.4, 130.1, 129.1, 128.4, 125.9, 52.3, 33.2, 31.7, 22.7, 14.3; IR (film) 2956, 2929, 2987, 2856, 1723, 1607, 1457, 1435, 1413, 1310, 1279, 1191, 1178, 1109, 1017, 969, 867, 761  $\text{cm}^{-1}$ ; HRMS (CI+)  $[\text{M}+\text{H}]^+$  found 219.1393,  $\text{C}_{14}\text{H}_{19}\text{O}_2$  requires 219.1385.

**2-Methylbiphenyl (Table 3, entry 1).** Prepared according to the general procedure from 2-methyl-*N,N,N*-trimethylanilinium trifluoromethanesulfonate (47 mg, 0.157 mmol) and phenylboronic acid (38 mg, 0.314 mmol). Purification by flash chromatography (2% EtOAc/Hexanes) gave the title compound as a colourless oil in 89% yield (23.5 mg, 0.140 mmol), which had physical data identical in all respects to that previously reported.<sup>5</sup>

**2-Methoxybiphenyl (Table 3, entry 2).** Prepared according to the general procedure from 2-methoxy-*N,N,N*-trimethylanilinium trifluoromethanesulfonate (50 mg, 0.157 mmol) and phenylboronic acid (38 mg, 0.314 mmol). Purification by flash chromatography (5% EtOAc/Hexanes) gave the title compound as a colourless oil in 84% yield (24.3 mg, 0.132 mmol), which had physical data identical in all respects to that previously reported.<sup>6</sup>

**3-Methoxybiphenyl (Table 3, entry 3).** Prepared according to the general procedure from 3-methoxy-*N,N,N*-trimethylanilinium trifluoromethanesulfonate (50 mg, 0.157 mmol) and phenylboronic acid (38 mg, 0.314 mmol). Purification by flash chromatography (5% EtOAc/Hexanes) gave the title compound as a colourless oil in 96% yield (27.6 mg, 0.151 mmol), which had physical data identical in all respects to that previously reported.<sup>7</sup>

**4-*n*-Butoxybiphenyl (Table 3, entry 4).** Prepared according to the general procedure from 4-*n*-butoxy-*N,N,N*-trimethylanilinium trifluoromethanesulfonate (56 mg, 0.157 mmol) and phenylboronic acid (38 mg, 0.314 mmol). Purification by flash chromatography (3%

<sup>5</sup> Bei, X.; Turner, H. W.; Weinberg, W. H.; Guram, A. S.; Peterson, J. L. *J. Org. Chem.* **1999**, *64*, 6797.

<sup>6</sup> Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550.

EtOAc/Hexanes) gave the title compound as a colourless oil in 85% yield (30.3 mg, 0.133 mmol), which had physical data identical in all respects to that previously reported.<sup>8</sup>

**3,5-Dimethoxybiphenyl (Table 3, entry 5).** Prepared according to the general procedure from 3,5-dimethoxy-*N,N,N*-trimethylanilinium trifluoromethanesulfonate (50 mg, 0.157 mmol) and phenylboronic acid (38 mg, 0.314 mmol). Purification by flash chromatography (6% EtOAc/Hexanes) gave the title compound as a colourless oil in 92% yield (30.9 mg, 0.144 mmol), which had physical data identical in all respects to that previously reported.<sup>9</sup>

**Biphenyl-4-carboxylic acid methyl ester (Table 3, entry 6).** Prepared according to the general procedure from 4-(carboxylic acid methyl ester)-*N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and phenylboronic acid (38 mg, 0.314 mmol). Purification by flash chromatography (5% EtOAc/Hexanes) gave the title compound as a colourless oil in 93% yield (31.0 mg, 0.146 mmol), which had physical data identical in all respects to that previously reported.<sup>10</sup>

**Biphenyl-3-carboxylic acid methyl ester (Table 3, entry 7).** Prepared according to the general procedure from 3-(carboxylic acid methyl ester)-*N,N,N*-trimethylanilinium trifluoromethanesulfonate (54 mg, 0.157 mmol) and phenylboronic acid (38 mg, 0.314 mmol). Purification by flash chromatography (5% EtOAc/Hexanes) gave the title compound as a colourless oil in 94% yield (31.3 mg, 0.148 mmol), which had physical data identical in all respects to that previously reported.<sup>11</sup>

**3-Fluorobiphenyl (Table 3, entry 8).** Prepared according to the general procedure from 3-fluoro-*N,N,N*-trimethylanilinium trifluoromethanesulfonate (48 mg, 0.157 mmol) and phenylboronic acid (38 mg, 0.314 mmol). Purification by flash chromatography (3% EtOAc/Hexanes) gave the title compound as a colourless oil in 88% yield (23.8 mg, 0.138 mmol), which had physical data identical in all respects to that previously reported.<sup>12</sup>

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<sup>8</sup> Parrish, J. P.; Sudaresan, B.; Jung, K. W. *Synth. Commun.* **1999**, 29, 4423.

<sup>9</sup> Dol, G. C.; Kamer, P. C.; van Leeuwen, P. W. N. M. *Eur. J. Org. Chem.* **1998**, 359.

<sup>10</sup> Schneider, S.; Bannwarth, W. *Helv. Chim. Act.* **2001**, 84, 735.

<sup>11</sup> Kang, S.-K.; Kim, J.-S.; Yoon, S.-K.; Lim, K.-H.; Yoon, S. S. *Tetrahedron Lett.* **1998**, 39, 3011.

<sup>12</sup> Anklam, E.; Asmus, K.-D.; Robertson, L. W. *J. Fluorine Chem.* **1988**, 39, 209.